

No. 771,086



ISSUED Nov. 7, 1967  
CLASS 18-155

# CANADIAN PATENT

RECLAIMING SPANDEX YARN BY DISSOLVING, FILTERING  
AND DRY-SPINNING

BEST AVAILABLE COPY

James L. Dismore, Waynesboro, Virginia, U.S.A.

Granted to E. I. du Pont de Nemours and Company, Wilmington,  
Delaware, U.S.A.

APPLICATION No. 687,000  
FILED May 4, 1965  
PRIORITY DATE June 27, 1964 (378,505) U.S.A.  
No. OF CLAIMS 8

Vorlage nicht besser kopierfähig

771086

This invention relates to spandex yarns derived from metaxylylenediamine and is particularly directed to the reclaiming and utilization of waste and scrap resulting from the spinning of such spandex yarns.

5           In the conventional production of spandex yarns, substantial amounts of waste are produced. Thus, yarn produced which is outside of accepted physical limits, e.g. acceptable variations in denier, is rejected. Particularly, in the start-up of a spinning cell, cell temperatures and various  
10 metering pumps must be adjusted so that yarn having the desired optimum properties is obtained. Any yarn outside specified limits is usually scrapped. Similarly, at the time of doffing of the spinning bobbins as well as in rewinding operations involving spandex yarns, varying amounts of waste are obtained  
15 and discarded.

This invention provides a method for satisfactorily reclaiming waste spandex yarn while at the same time affording a process for producing spandex having superior fume-fade resistance and whiteness retention.

20           The advantages of this invention are attained by a process which comprises dissolving a first spandex yarn in a solvent to form a solution thereof, filtering the solution to remove solids therefrom, and forming a second spandex yarn by extruding the solution through an orifice and evaporating the  
25 solvent, the first and second spandex yarns each being the extruded, linear polymeric reaction product of a polyglycol, a diisocyanate, and metaxylylenediamine. As an added advantage of the invention, the spinning of a spandex filament a second time does not adversely affect whiteness retention or physical  
30 properties such as tenacity and elongation. In fact, for the most part, a definite improvement in whiteness retention can be observed as compared to spandex spun only once.



771086

As indicated above, the spandex yarn to which this invention pertains is the reaction product of a polyglycol, a diisocyanate, and metaxylylenediamine. As is well known in the art, spandex fibers are composed of segmented polyurethanes which contain segments of a high-melting, crystalline polymer alternating with segments of a low-melting, amorphous polymer. In this invention, the crystalline segment is a polyurea derived from metaxylylenediamine and an organic diisocyanate. The organic diisocyanate is not critical, and any of those disclosed in the prior art pertaining to spandex may be used. The preferred diisocyanate is p,p'-methylenediphenyl diisocyanate. The amorphous segment of the segmented polyurethane is similarly well known in the art and may be derived from a low-melting polyglycol, for example, a polyester glycol or a polyether glycol, as is also well known in the art. More specifically, U. S. Patents 2,929,804, 2,957,852 and 3,097,192 disclose spandex fibers formed of a polymeric reaction product of a polyglycol, a diisocyanate and a diamino compound. The yarns suitable for treatment in accordance with the present invention may be formed by the use of metaxylylenediamine as the diamine in the processes described in those patents. As further disclosed in the aforementioned patents, the preferred spandex filaments for treatment in accordance with the present invention display elongation at the break in excess of 200%, elastic recovery (or tensile recovery) above about 90%, and stress decay below about 20%. The spandex yarns produced by the process of this invention, e.g. from solutions of waste spandex, should similarly exhibit such property levels.

The drawing illustrates in the form of a flow diagram the process of the invention. Specific details of the various steps thereof will be described in the paragraphs which follow.

771086

In the practice of this invention, the waste spandex yarn is dissolved in a solvent to form a solution. Hence the spandex must possess a substantially linear polymeric structure so that it will be soluble in the solvents used. The  
5 term "substantially linear" is not intended to exclude polymeric structures which have branches extending out from the main polymer chain. Spandex yarns having an intrinsic viscosity not in excess of about 2 will normally be sufficiently soluble to enable reclamation.

10 The solvents which are suitable in the process of this invention are the lower dialkylamides of the lower fatty acids. The suitable solvents include dimethylformamide, dimethylacetamide, diethylformamide, dimethylpropionamide, and diethylacetamide. The preferred solvent is dimethylacetamide.  
15 The solution of the waste spandex in the solvent may be formed in any convenient manner, for example, by agitation of the mixture at room temperature. In general the temperature of the solution should not be allowed to exceed 60°C., and the concentration of waste yarn in the solution should not exceed  
20 25% by weight.

In the process of forming the solution, it is advantageous to initially effect some sub-division of the waste yarn, such as by chopping the material as-obtained into short lengths. The chopped yarn is then weighed, and an appropriate  
25 amount of solvent is added such that the concentration is less than the 25% limit mentioned previously. The waste spandex is then permitted to soak in the solvent for a moderate amount of time, for example, an hour, prior to agitation. It is found that the step of soaking the yarn prior to agitation is not  
30 absolutely necessary, but facilitates the ease of preparing

771086

a solution of the waste spandex. If sufficiently rapid agitation of the solvent and yarn is available, no specified soaking period is necessary. Suitable agitators include, for example, screw-type and disc-type agitators. Agitation is continued until the yarn is substantially all dissolved. The period of agitation depends on obvious variables, such as the size of the tank, dimension and form of the agitators, viscosity of the solution, and speed of agitation. The speed of agitation is adjusted so that the solution temperature does not exceed 60°C.

After the solution of waste spandex is obtained, it is then filtered to remove any small particles remaining undissolved. It is essential to remove such particles in order to avoid clogging of spinneret orifices and other spinning difficulties in the subsequent forming of spandex filaments. Conventional filters such as an ordinary filter press may be used.

The filtered solution of waste spandex is then ready for spinning. It may, of course, be extruded as obtained, undiluted with other polymer. Alternatively, it is advantageously first blended with a filtered solution of spandex polymer derived from material that has never before been spun. In order that the advantages of this invention may be achieved, the blending of a solution of waste spandex yarn with a solution of un-spun or virgin spandex polymer should be carried out so that the waste spandex constitutes at least 5% and up to half or more by weight of the total polymeric solids in the combined solutions. The blending of the solutions may be accomplished in any desired manner. For practical operation of a commercial spandex plant, blends containing from about 15% to about 20% of waste based on the total polymeric solids are most advantageous. A blend containing about 15% waste is preferred.

771086

10  
\*  
It is known that oil-based finishes, for example, as described in U S. Patent 3,039,895, are commonly used on spandex yarns and are applied directly below the spinning cell before winding up the spun filaments on a bobbin. Waste yarn, therefore, ususally contains an oil-based finish. In the practice of the instant process such finishes may first be removed, if desired. Generally, finish removal is not necessary. If finish removal is desired, the chopped, waste yarn may be washed thoroughly with a suitable organic solvent, for example, acetone, and then rinsed with water and dried thoroughly before it is dissolved according to this invention.

20  
After the filtered solution of waste spandex has been prepared and optionally blended with a solution of virgin polymer, the solution is then extruded in a dry-spinning cell in the conventional manner for the production of spandex filaments. The filaments so obtained generally display somewhat greater whiteness retention and resistance to fume fading than does spandex containing no waste yarn. It is significant that the mechanical properties, e.g., tenacity and elongation, of spandex  
30  
yarns are not adversely affected by the process. Perhaps the most important advantage of this invention, however, is that it provides a useful process for effecting substantial economy by reclamation of waste in the commercial production of spandex filaments.

This invention will be further illustrated, but is not intended to be limited, by the following examples in which parts and percentages are by weight unless otherwise specified.

"Intrinsic viscosity" as employed herein refers to the limiting value, as the concentration approaches zero, of the  
30  
expression

$$\frac{n - n_0}{n_0 c}$$

771086

in which  $n$  is the viscosity of a dilute solution of the polymer,  $n_0$  is the viscosity of the solvent (hexamethylphosphoramide) in the same units and at the same temperature, and  $c$  is the concentration in grams of the polymer per 100 ml. of solution.

The degree of yellowness, referred to in the examples as "b" value, is determined from colorimetric data obtained by analyzing continuous filament samples which are about three inches square. The reflectance ratios of the samples in the green and blue filter settings of a colorimeter are measured, using a Model IV Color Master Differential Colorimeter, manufactured by Manufacturing Engineering and Equipment Company, Hatboro, Pennsylvania, and calibrated against the manufacturer's standard reference plates and the National Bureau of Standards' certified reflectance plates. Three readings are taken on each of the samples, one of the measurements for the filament sample being made with the sample rotated 90° from the position of the first reading. The "b" values are then calculated from the average of three readings, using the following formula

$$b = 42.34 G^{1/3} B^{1/3}$$

where  $G$  represents the reflectance ratio with the green filter and  $B$  represents the reflectance ratio with the blue filter. In the examples the "b" values are reported in terms of " $\Delta b$ "; that is, the difference in the degree of yellowness as measured before and after exposure to or treatment with a chemical agent or other medium which is known to deleteriously affect the color of spandex yarns. The treatments thus simulate conditions that a fabric formed of spandex fibers could be expected to encounter in normal usage. Before such an exposure the samples will typically have a "b" value below 1.0. It will be understood that the lower the " $\Delta b$ " value, the greater the whiteness retention.

771086

EXAMPLE I

Polytetramethylene ether glycol of molecular weight about 2000 and p,p'-methylenediphenyl diisocyanate are intimately mixed in the ratio of 2 mols of diisocyanate per mol of polyether glycol and are reacted at about 96°C. for 90-150 minutes to yield an isocyanate-terminated polyether. The isocyanate-terminated polyether, cooled to below 45°C., is conducted at a rate of 17.5 parts per hour into a mixer, and a stream of N,N-dimethylacetamide is added at 27.6 parts per hour. The mixture (39% solids) is discharged continuously into a pipeline and conducted to a second mixer having 0.06 second holdup time, in which it is intimately mixed with a stream of dimethylacetamide containing 9.1 weight per cent metaxylylenediamine and 0.6 weight per cent diethylamine, added at a total rate of 10.3 parts per hour. The mixture passes to a second mixer where it is agitated for 3-4 minutes at a temperature of 40°C. to 90°C. The emerging polymer solution contains approximately 33.7% solids and has a viscosity of 1450 poises at 40°C. The polymer has an intrinsic viscosity of 1.27. To the polymer solution are added a slurry of titanium dioxide in dimethylacetamide, a solution of poly-(N,N-diethyl-beta-aminoethyl methacrylate) in dimethylacetamide and a solution of 4,4'-butylidenebis-(6-t-butyl-m-cresol) in dimethylacetamide such that the final mixture contains 5%, 5%, and 1%, respectively, of each additive, based on the elastomeric solids.

The foregoing mixture is heated to a temperature of 70°C. and spun into a dry-spinning column in the conventional manner. The individual filaments are brought into contact within the column and adhere to one another to give a coalesced multifilament of about 410 denier (45.5 Tex). Upon emergence



771086

from the column, the coalesced multifilament is treated with about 3% by weight of a finish consisting of 10% polyamylsiloxane and 90% polydimethylsiloxane. The spandex yarn has an intrinsic viscosity below 2.

5 A portion of the foregoing spandex yarn representing waste is chopped into lengths of about 5 cm. and added to dimethylacetamide such that the concentration of yarn is 25%. After a soaking period of 60 minutes, the yarn is agitated for 120 minutes at a temperature of 35°C. The solution is filtered through sheets of cellulose pulp (Buckeye Type 12F7), and the filtrate is blended with a fresh batch of spinning solution prepared as described in the first paragraph of this Example. The quantities blended are such that the waste spandex constitutes 37% by weight of the total solids of the combined solutions.

10 The solution blend is then dry-spun as before, and the resulting product is compared with a sample of the same spandex which contains no previously spun yarn (control). Skeins of the yarns are measured for color in terms of "b" value and are then exposed to chlorine by immersing each skein in 6012 ml. of an aqueous solution containing 70 parts per million active chlorine at 73°C. The skeins are moved about in the bath and after 20 minutes are removed, rinsed with cold water, and dried thoroughly and again measured for color. The results are as follows:

	<u>Δb</u>
Sample containing 37% waste	5.8
Control	10.9

25 Another sample of the spandex is washed with isopropyl alcohol to remove the finish and then blended with a spinning solution as in the third paragraph of this Example. An additional blend is similarly made except that the finish

## 771086

is not removed from the waste yarn. Both solutions contain 5% by weight of the waste yarn. These mixtures are dry-spun and tested for chlorine resistance as before. Results are as follows:

5		<u><math>\Delta b</math></u>
	Sample containing 5% waste	3.7
	Sample containing 5% waste free of finish	4.7
	Control	9.6

### EXAMPLE II

10 Spandex yarn of 280 denier (31 Tex), prepared as described in Example I, is blended with fresh spinning solution so that the solids of the combined solution comprises 15% by weight of previously spun yarn. Samples are dry-spun as before. A sample of the yarn from the blended solution is exposed to malonaldehyde vapors at room temperature for 15 min. 15 A control containing no previously spun yarn is simultaneously exposed under the same conditions. The samples are measured for color both before and after exposure. The following results are obtained:

20		<u><math>\Delta b</math></u>
	Sample containing 15% waste	12.8
	Control	16.4

Another sample of previously spun yarn is dissolved in fresh dimethylacetamide as described in Example I and dry-spun again to give filaments of 420 denier (46.6 Tex) without any blending with virgin polymer solution. The following results are obtained:

25		<u><math>\Delta b</math></u>
	Sample containing 100% waste	7.4
30	Control	15.1

771086

EXAMPLE III

Another sample of the blended spinning solution of Example II containing 15% of previously spun yarn is dry-spun in the usual manner to give spandex filaments of 420 denier (46.6 Tex). The sample is exposed to a synthetic atmosphere containing air, nitrogen dioxide, sulfur dioxide, 2-pentene, and nitrogen, which atmosphere is considered to be typical of smog. While exposed, the sample is irradiated for three hours by a combination of ultraviolet and visible light. A similar yarn containing 15% by weight of previously spun, finish-free yarn is also similarly exposed together with a control. The samples are measured for color, both before and after exposure. The following results are obtained:

	<u><math>\Delta b</math></u>
15 Sample containing 15% of waste yarn free of finish	4.7
Sample containing 15% of waste yarn with finish	5.5
Control	7.1

20 As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments thereof except as defined in the appended claims.

771086

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Method for producing a spandex yarn comprising the steps of dissolving a first filament in a solvent to form a solution thereof, filtering the solution to remove solids therefrom, and forming a second filament by extruding said solution through an orifice and evaporating the solvent, said first and second filaments each being the extruded linear polymeric reaction product of a polyglycol, a diisocyanate, and metaxylylenediamine.

2. Process of Claim 1 wherein said solvent is a lower dialkylamide of a lower fatty acid.

3. Process of Claim 1 wherein said solvent is dimethylacetamide.

4. Process of Claim 1 wherein said first filament has an intrinsic viscosity not in excess of about 2.

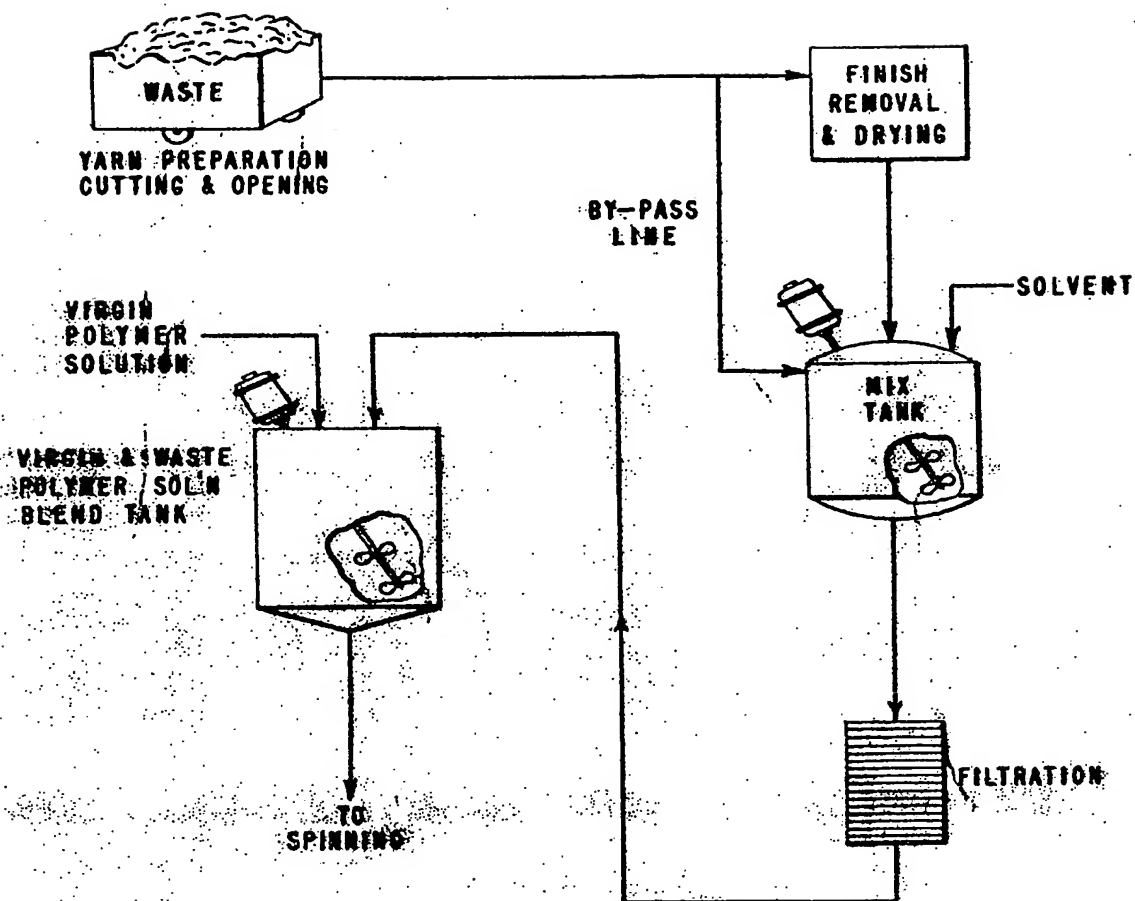
5. Process of Claim 1 wherein said solution contains less than about 25% of said first filament and is formed at a temperature not in excess of about 60°C.

6. Process of Claim 1 wherein said first filament is from waste yarn.

7. In a process for producing spandex yarn by extruding through an orifice in a dry-spinning cell a solution of the linear polymeric reaction product of a polyglycol, a diisocyanate, and metaxylylenediamine in a solvent comprising a lower dialkylamide of a lower fatty acid, the improvement wherein said reaction product is comprises of 50 to 95% by weight of un-spun polymer and 5 to 50% by weight of polymer obtained by dissolving a previously spun spandex yarn in a solvent to form a solution, and filtering the solution to remove solids therefrom.

8. Process of Claim 7 wherein the two said polymers comprise 80 to 85% and 15 to 20% by weight, respectively.





INVENTOR

*James L. Blendale*

PATENT AGENT

*NW McKinnis*

This Page is inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record

## BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images  
problems checked, please do not report the  
problems to the IFW Image Problem Mailbox**